

## Treatment of Araib Acidic Mine – Influenced Water with Sudanese Trona Deposits (ATROUN)

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**ABSTRACT:** The investigation of six samples of Acidic Mine-Influenced Water (AMIW) from Ariab area, Red Sea Hills, northeastern part of Sudan, showed high pollution signs. The waste water parameters examined showed that, the acidity, sulphate contents, total iron Fe, copper Cu, zinc Zn, manganese Mn, cobalt Co and cadmium Cd were all highly above the effluent discharge limits. Composite trona (atroun) sample from northwest Darfur, which is used for treatments, was analyzed for the major and minor constituents, the analysis showed that the total alkalinity was 123400 mg of  $\text{CaCO}_3/\text{dm}^3$ , sand and insoluble matter of 10.75%, sodium carbonate content of 33.14%, sodium bicarbonate of 6.57%, sodium sulphate of 8.23% and sodium chloride content of 23.34% w/w. The contents of heavy and environmentally toxic elements (such as Fe, Co, Ca, Cd, Cu, Zn, Mn, and Pb) were all below the effluent discharge limits. The treatment of Ariab AMIW with Atroun solution at pH 10.0 for 2- and 24- hour settling periods showed promising signs as treatment alkali and many parameters were brought down to the threshold limits specified by effluent discharge standards. In the treated samples, the total Fe was 100% removed, Cd and Co were removed to values below the limits. High removal percentages of Cu, Mn and Zn were obtained in most of the treated samples in both settling periods, though, some of the values didn't conform to standard effluent limits. Unfortunately the sulphate content however was increased more than that found in the original samples due to the introduction of sulphate from impure atroun used for the treatment.

**KEYWORDS:** *Ariab, acid mine-influenced water, trona, acidity, pollution, toxic elements.*

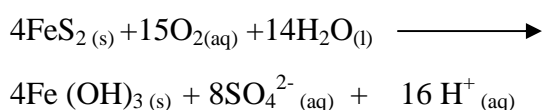
### INTRODUCTION

Mining industry is considered as one of the most environmental pollutants through all human activities. Mining activities produce huge amounts of solid waste such as rocks, soil and tailings, air pollution with toxic gases and dust particulates in addition to mine-influenced water (MIW). Mine-influenced water can be defined as the natural mine underground water, or the rain water that falls on the mine waste and disposal and dissolves some of the waste constituents, <sup>[1]</sup>. Base metal and Coal mining industries are considered as

the most mine-influenced water producing activities. The mining of base metals such as copper, lead, zinc, antimony and gold is always accompanied by different sulphidic rocks and fluids. Sulphide-bearing minerals like Pyrite, Pyrrhotite, Marcasite, Galena, Chalcopyrite and Arsenopyrite are the dominant ore minerals accompanying the production of these metals. Iron sulphide minerals, pyrite, Marcasite and Pyrrhotite are the common solid waste in the coal mining industry. Gold is extracted mainly in Ariab area from gossans and silica barite rocks in the oxidation zone of the massive sulphides <sup>[2, 3]</sup>.

Acidic mine-influenced water (AMIW) , commonly referred to as acid mine drainage (AMD) is a natural consequence of many mining activities or any other large earth disturbance that exposes sulphur containing minerals to oxygen, water and microorganisms. [4,5].

The production of AMIW is a multi step process, the chemical equations of these steps can be summarized in the following equation:



Chemically, the products of the interaction between mine wastes and minerals are mainly ( $\text{SO}_4^{2-}$ ), ( $\text{H}^+$ ) and metal ions largely iron (Fe).

Treatment of AMIW is the final step carried after the control and prevention methods and techniques failed to stop or reduce the toxic leached metals and the corrosive acidic drainage. The target of AMIW treatment is to eliminate or reduce the impacts of the mine effluents on the receiving environment to levels that meet the discharge limits issued by the legal authorities.

Treatment of AMIW can be broadly divided into passive and active types. Passive treatment systems (PTS) which refers to the methods and technologies that rely on biological, geochemical and gravitational processes and don't require the constant input of chemical reagent and operating.[6]. Active treatment systems of AMD are the treatment methods that utilize alkalis and alkaline materials to neutralize the acidity of AMD and precipitate the leached metal ions by increasing the pH of AMD.[7].

Many chemicals are normally used to neutralize AMD with varying degrees of efficiency and cost such as limestone ( $\text{CaCO}_3$ ) , hydrated lime ( $\text{Ca}(\text{OH})_2$ ) , pebble quicklime ( $\text{CaO}$ ) , soda ash

( $\text{Na}_2\text{CO}_3$ ) , caustic soda ( $\text{NaOH}$ ) and ammonia ( $\text{NH}_3$ ).[8]

Many sodium carbonate minerals were discovered worldwide. The most common minerals are the followings: trona which is natural sodium sesquicarbonate, ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ), nahcolite, which is natural sodium bicarbonate ( $\text{NaHCO}_3$ ), thermonitrite, which is sodium carbonate monohydrate ( $\text{Na}_2\text{CO}_3 \cdot \text{H}_2\text{O}$ ) and natron, which is sodium carbonate decahydrate ( $\text{Na}_2\text{CO}_3 \cdot 10\text{H}_2\text{O}$ ). Only trona is of commercial interest.

Trona is a relatively rare, non-metallic mineral, ( $\text{Na}_2\text{CO}_3 \cdot \text{NaHCO}_3 \cdot 2\text{H}_2\text{O}$ ). The pure material contains 70.39 % sodium carbonate and by calcination the excess  $\text{CO}_2$  and water can be driven off, yielding natural soda ash. Trona gets its name from a discarded Arabic word for native salt, "tron", which is derived from the word "natron".

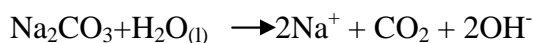
Natural soda ash resources (either trona or sodium carbonate-rich brines) were found primarily in the U.S.A., Mexico, Russia, Kenya, China and Turkey [9]. The largest known deposits of trona found in prehistoric alkaline lakebed in the southwest Wyoming and now called Green River Basin, U.S.A., where about 47 billion metric tons of identified soda ash resources could be recovered from the 56 billion tons of bedded trona and the 47 billion tons of interbedded or intermixed trona and halite. Trona mining accounts for 90% of the U.S. production of soda ash ( $\text{Na}_2\text{CO}_3$ ) [10, 11].

The other important resources are Magadi Lake, in Kenya and Texaco brines in Mexico. In Sudan, trona, atroun, are found north and northwest in many locations: at Abu hamad, 200 kilometers northwest of Ariab area, River Nile state, north Darfour state at many old oasis,

and old dry lakes such as El Nakhiela, El Slaim, Alga'a and Al Dalieb. <sup>[12,13]</sup>.

When atroun dissolves in water, it releases three moles of alkalinity as OH<sup>-</sup>, two from Na<sub>2</sub>CO<sub>3</sub> and one from NaHCO<sub>3</sub>, which are capable of neutralizing three moles of AMIW acidity as explained by the following equations:

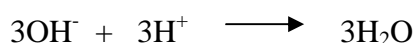
Dissolution of sodium carbonate,



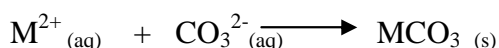
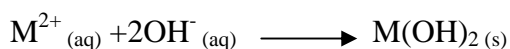
Dissolution of sodium bicarbonate,



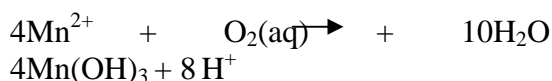
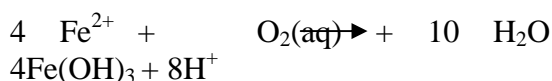
Acidity neutralization ,



Soluble metal ions can be precipitated either as metal hydroxides or carbonates as in the following equations:



The following equations are examples of precipitated metal hydroxides:



Each country issued effluent discharge limits standards depending on the geochemical nature of minerals at the mine site and the tolerance of the receiving environment to the acidity and elemental pollutants carried by the AMIW such as the Sudanese standard thresholds for industrial wastewater <sup>[14]</sup>, the SABS License Limit for effluent discharge, <sup>[15]</sup> and WHO International drinking water standards, max. Allowable conc <sup>[16]</sup>.

The main objective of this work is to remove the toxic environmental pollutants in Ariab mine-influenced water to environmentally safe levels by neutralizing the acidity, rising the pH and precipitating the toxic and heavy metal ions using atrona deposits (Atroun) as local alkaline mineral resource.

## MATERIALS and METHODS

Six composite samples of mine-influenced water were collected from mining sites of Ariab Mining Company, at Ariab area, Red Sea hills, and northwestern part of the Republic of Sudan. Each sample was a composite of 8 subsamples from different depths and location from the ponds at the bottom of each mine. The samples were analyzed according to standard methods of analysis of waste water, <sup>[17]</sup>. pH-value was measured at 25°C using Hannah pH meter. Sulphate was determined gravimetrically using barium chloride method. Total iron was analyzed volumetrically using standard potassium dichromate and barium diphenylamine sulphonate as indicator <sup>[18]</sup>.

Copper, zinc, manganese, cobalt, cadmium, calcium and lead were determined spectrophotometrically using Schematzou AAS – 6800 instrument. All readings were made in duplicates and the average reading was taken. Standard reference samples were prepared from standard metal solutions specially for atomic absorption to check the efficiency and accuracy of the whole analytical process.

A composite atroun sample, that was collected from West Darfour state, was brought from Omdurman market, crushed, homogenized to pass 2.36 mm sieve, dissolved in distilled water and chemically analyzed for the major and minor constituents.

Sand and insoluble materials were determined gravimetrically by dissolution in distilled water and filtration, dried at  $105 \pm 2$  °C and weighed. Carbonates and bicarbonates were determined volumetrically using standard hydrochloric acid, phenolphthalein and methyl orange as indicators<sup>[19]</sup>.

Sulphate was determined gravimetrically. Sodium chloride was determined volumetrically using Volhard's method. Trace metals were analyzed by atomic absorption spectrophotometry.

Atroun solution was prepared by dissolving one kilogram of the composite atroun sample in 3 decimeters of distilled water. The water insoluble materials like sand, clay and organic matter were filtered through Buchner funnel using Whatman filter paper No. 41 under suction and kept at 4°C for further analysis and treatment.

The total alkalinity of atroun solution and the alkalinities of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) were determined titrimetrically using standard sulphuric acid (0.500 M) and methyl orange and phenolphthalein as indicators<sup>[20]</sup>.

The previous atroun (trona) solution was used for the treatment of Ariab AMIW samples as follows; Four aliquots of 5  $\text{cm}^3$  of each of sample 1, 2, 3, 4, 5 and 6 were pipetted in 100  $\text{cm}^3$  beaker and diluted to 20  $\text{cm}^3$  with deionized water. The four aliquots of each sample (aliquot 1, 2, 3, 4) were treated with different volumes of Atroun solution according to their inherent acidity with vigorous stirring using magnetic stirrer to a pH value of 4, 6, 8 and 10. The treated aliquots were allowed to settle for two hours and then centrifuged in a polyethylene tube (100  $\text{cm}^3$ ) at 4500 round per minute for 15 minutes. The pH of the treated solution was determined<sup>[17]</sup>.

The supernatant was slowly decanted, filtered, its pH was determined, then neutralized, acidified with 2  $\text{cm}^3$  of concentrated nitric acid (69.0%), completed to the mark in 100  $\text{cm}^3$  volumetric flask with deionized water and analyzed for sulphate content after two hour settling period. The same treatment was repeated for the same samples and aliquots, but the settling time was extended to 24 hours.

Total iron was analyzed volumetrically using standard potassium dichromate method for solutions treated at pH 4 and 6. Treated solutions to pH 8 and 10 that contain traces of iron however, were analyzed by atomic absorption spectrophotometry. Mn, Zn, Cu, Cd and Co were determined also by atomic absorption spectrophotometer. The results obtained after 2 and 24 hour settling periods are shown in tables 5, and 6, respectively.

### Statistical Analysis

Each one of the composite six samples was made up of 8 subsamples from different locations and depths of the mine ponds. Each chemical test was repeated two times at least and the average result was taken.

### Results and Discussion

The total alkalinity of atroun solution was found to be 123400  $\text{mg}/\text{dm}^3$  as  $\text{CaCO}_3$  and the alkalinities of sodium carbonate ( $\text{Na}_2\text{CO}_3$ ) and sodium bicarbonate ( $\text{NaHCO}_3$ ) were found to be 110000  $\text{mg}/\text{dm}^3$   $\text{CaCO}_3$  and 13400  $\text{mg}/\text{dm}^3$   $\text{CaCO}_3$ , respectively.<sup>[20]</sup>

The investigation showed that Ariab AMIW samples were highly acidic effluents which had negative impact on the neighboring environment. The low pH values and high acidities rendered Ariab AMIW as corrosive effluents and increased the tendency of the contaminated water to dissolve toxic and

heavy metals in the adjacent minerals and rocks. High dissolved metal ions load in the samples under study was a result of the dissolution of mine minerals.

Extraordinary content of iron , zinc , copper and manganese proved the aggressiveness of the effluents. Table 1 lists the results.

*Table 1: Chemical analysis of the six acid mine-influenced water samples.*

parameter	S.1	S.2	S.3	S.4	S.5	S.6
pH-value at 25 °C	01.88	01.62	02.44	01.86	01.77	01.30
Total Acidity in mg CaCO <sub>3</sub> / dm <sup>3</sup> , x10 <sup>5</sup>	02.25	01.90	2.18	02.18	02.32	00.43
SO <sup>-2</sup> <sub>4</sub> in mg/ dm <sup>3</sup> ,x 10 <sup>5</sup>	02.26	01.97	2.03	02.12	02.35	00.40
Fe in mg/ dm <sup>3</sup> , x 10 <sup>4</sup>	02.16	08.99	7. 80	08.46	10.40	00.99
Co in mg/ dm <sup>3</sup>	50.00	44.66	48.81	40.52	47.62	04.48
Ca in mg/ dm <sup>3</sup>	01.75	01.70	01.65	01.25	00.85	02.00
Cd in mg/ dm <sup>3</sup>	12.16	08.04	06.84	05.26	07.18	10.65
Cu in mg/ dm <sup>3</sup> , x10 <sup>3</sup>	01.10	01.07	00.56	00.28	00.49	00.50
Zn in mg/ dm <sup>3</sup> ,x 10 <sup>3</sup>	03.35	02.90	02.66	01.80	02.56	02.94
Pb in mg/ dm <sup>3</sup>	00.00	00.00	00.00	00.00	00.00	00.00
Mn in mg/dm <sup>3</sup> , x10 <sup>2</sup>	05.70	02.25	02.10	02.26	02.43	02.75

The local atroun mineral which is an impure trona mineral that constitutes a mixture of sodium carbonate and bicarbonate, is contaminated with many other impurities such as sodium chloride, sulphate, sand and other insolubles in addition to traces of metals such as Mn, Zn, Fe and Cu. Table 2 shows the constituents of atroun. The carbonate and

bicarbonate imparted an alkalinity of 123400 mg CaCO<sub>3</sub>/dm<sup>3</sup> to the treating alkaline solution. The solution was used instead of solid atroun to avoid the armoring due to the precipitation of the metal hydroxides on the reactive surface, in addition to the ease of mixing and reaction.

Table 2: Major and minor constituents of atroun (trona)

Test No.	Atroun constituent	Results in percent (m/m) and concentration
1	Sand and insoluble materials	10.75 % (m/m)
2	Sodium carbonate as Na <sub>2</sub> CO <sub>3</sub>	33.14 % (m/m)
3	Sodium bicarbonate as NaHCO <sub>3</sub>	06.57 % (m/m)
4	Sodium sulphate as Na <sub>2</sub> SO <sub>4</sub>	08.23 % (m/m)
5	Sodium chloride as NaCl	23.34 % (m/m)
6	Total Alkalinity (as CaCO <sub>3</sub> )	123400mg /dm <sup>3</sup>
7	Manganese, Mn	0.20 mg/ dm <sup>3</sup>
8	Lead, Pb	0.00 mg/ dm <sup>3</sup>
9	Iron, Fe	0.88 mg/ dm <sup>3</sup>
10	Cadmium, Cd	0.01 mg/ dm <sup>3</sup>
11	Zinc, Zn	0.11 mg/ dm <sup>3</sup>
12	Copper, Cu	0.06 mg/ dm <sup>3</sup>
13	Cobalt, Co	0.00 mg/ dm <sup>3</sup>
14	Calcium, Ca	0.00 mg/ dm <sup>3</sup>

Neutralization of Ariab AMIW with atroun solution precipitated soluble metal ions as hydroxides, carbonates and many other mixed compounds. The amount of sludge precipitated and hence the metal content was a function of pH, so, increasing the pH to about 9, reduced the metal load of nearly all elements to more than 95% in both settling periods.

It was found that the sulphate content of the treated AMIW had increased in direct proportionality to the increase in pH depending on the amount of Atroun solution added to reach the required value. The atroun solution used for the neutralization and precipitation of the AMIW metal ions contained considerable sulphate content as Na<sub>2</sub>SO<sub>4</sub> (8.23 %),

which introduced additional sulphate to the neutralized samples. Consequently, an increase in the net sulphate content of the treated AMIW samples, especially at pH 8 and 9, were found to be even higher than those already found in the original samples. This trend was followed when the treated solutions were left to settle for 2 and 24 hour except sample 6 in the 24 hour settling period, at the end of which the sulphate content was found to be slightly lower than the original value. This behavior may be attributed to the chemical composition of the sample, adsorption and coprecipitation of sulphate ion during prolonged standing. The sulphate content of the treated samples at 2 hour settling period was less than that detected in 24 hour period in all treated

samples excluding sample 6. Dissolution of amorphous iron hydroxy sulphate and desorption of adsorbed sulphate may be responsible for this behavior, as listed in table 3.

The utilization of impure neutralizing materials may, however, incorporates

some pollutants in the treated effluent. An increase in sulphate, calcium, pH, arsenic, selenium, boron, sodium, and potassium were observed in a study of the interaction between flue gas desulphurization by-product and acid mine drainage. <sup>[21]</sup>

*Table 3: Sulphate content and pH of a group of treated AMIW samples*

Sample No.	Treatment pH	SO <sub>4</sub> content in mg/dm <sup>3</sup> at 2- hour period	Sample No.	Treatment pH	SO <sub>4</sub> , mg/dm <sup>3</sup> at 24- hour period
S.1	pH 4	217711	S.1	pH 4	231386
S.1	pH 6	213256	S.1	pH 6	233155
S.1	pH 8	228252	S.1	pH 8	262204
S.1	pH 10	244255	S.1	pH 10	310655
S.2	pH 4	194144	S.2	pH 4	200072
S.2	pH 6	199249	S.2	pH 6	211277
S.2	pH 8	215563	S.2	pH 8	232974
S.2	pH 10	230405	S.2	pH 10	271763
S.3	pH 4	224462	S.3	pH 4	228256
S.3	pH 6	223475	S.3	pH 6	230239
S.3	pH 8	234025	S.3	pH 8	278357
S.3	pH 10	282707	S.3	pH 10	289656
S.4	pH 4	187388	S.4	pH 4	210781
S.4	pH 6	209631	S.4	pH 6	212303
S.4	pH 8	248853	S.4	pH 8	250662
S.4	pH 10	275338	S.4	pH 10	279675
S.5	pH 4	252979	S.5	pH 4	230696
S.5	pH 6	254956	S.5	pH 6	233569
S.5	pH 8	268425	S.5	pH 8	273655
S.5	pH 10	337103	S.5	pH 10	341963
S.6	pH 4	052074	S.6	pH 4	042524
S.6	pH 6	055086	S.6	pH 6	034445
S.6	pH 8	059885	S.6	pH 8	043016
S.6	pH 10	061483	S.6	pH 10	052244

It was found that iron, as  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  ions, which constituted the major contaminating element in the AMIW of Ariab mines, was fortunately 100% removed in the atroun treatment even at pH 8 in all samples during both settling periods. In case of sample 6 Atroun neutralization removed iron completely at all studied pH values even at pH 4 during both settling periods. This proved that atroun is an efficient treating agent for low and moderate AMIW acidity and metal load. The removal of iron at pH 8 and 10 can be attributed to the precipitation

of iron carbonates as ferrous carbonate ( $\text{FeCO}_3$ ), in addition to the precipitation of other iron hydroxide and hydroxy sulphate compounds.

At pH 10 atroun treatment removed more than 98.0% of manganese ions in the samples 1, 2, 3, 4 and 5, during the settling period of two hours, though at pH 4 and 6, the concentration of manganese, during the same settling period, was not decreased appreciably. At pH 8 considerable removal of manganese was achieved during both treatment settling periods, except in sample 6 where only 95.45% and 94% of manganese were removed during the 2- and 24- hour settling periods, respectively. In their study on pH, dissolved oxygen and adsorption effect on metal removal in anaerobic bioreactor, Mark. Willow and Ronald Cohen, [22] found that, the removal of manganese is increasingly inefficient if the manganese ion oxidation state does not favor adsorption and the low pH is not appropriate, with the result that adsorption is no longer effective in the removal of manganese.

In aerobic natural waters, zinc forms complexes with numerous anions including  $\text{Cl}^-$ ,  $\text{SO}_4^{2-}$ ,  $\text{OH}^-$ , and  $\text{CO}_3^{2-}$ [23]. Those which influence solubility are the carbonate and the hydroxyl ions. Below pH of about 7.5, zinc carbonate is the

most insoluble form; as pH is increased, a hydroxy-carbonate mineral (hydrozincite) becomes controlling. The highest removal efficiency for zinc occurs at pH values more than 7.5. At low pH values, about pH 6, sorption and surface precipitation on the growing oxide surface is the most likely the mechanism for removal. However, when high carbonate and hydroxide exists, high pH zones are formed in which hydrozincite might be formed. The hydrozincite solubility may be the controlling factor since the solubility product of hydrozincite depends on the concentration of  $\text{OH}^-$  and  $\text{CO}_3^{2-}$  [23]. The removal of zinc follows an increasing order with pH value, but the complete removal of it was not achieved even at pH 10, though more than 99.5% was removed. At higher pH values, the presence of zinc traces may be due to amphoteric nature of soluble zinc compounds. Table 4 and 5 show that some constituents of the soluble remaining zinc exceeded the limits specified by WHO standards. [16]. It was reported that the presence of carbonate  $\text{CO}_3^{2-}$  and hydroxide  $\text{OH}^-$  ions in solution provides suitable atmosphere for zinc ions to form several compounds which differ in their solubilities [24].

High removal of copper was achieved at pH 8 and pH 10 during both settling periods, indicating that copper removal favors the alkaline medium. The presence of carbonate ion might enhance the precipitation of copper as copper basic carbonates  $\text{CuCO}_3$ . $\text{Cu}(\text{OH})_2$  which increased the trend to precipitation.

Copper forms complexes with many ligands, but in this treatment medium, with relatively low organic matter, the most likely ligands for complexation were the hydroxyl and carbonate ions. Copper (II) solubility decreased with the increase in pH due to the formation of malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ) and tenorite ( $\text{CuO}$ ), reaching a minimum solubility at about pH 11. The removal of copper



could be attributed to many other different reasons, such as sorption and surface precipitation or both, surface precipitation was the result of the substitution of the foreign cation for the main ion (ferric ion) in the growing crystal structure. Cadmium had been removed to a high degree at pH 8, with a trend to redissolve again at pH 10, The best pH to get rid of cadmium is, therefore, 8. The tendency to redissolve may be due to the nature of cadmium carbonate compound formed during the precipitation, whereas  $\text{Cd}(\text{OH})_2$  is insoluble in alkaline medium. It was reported that increasing pH from 2 to 8

causes a sharp rise in Cd sorption for soils deficient in dissolved organic matter . This was attributed mainly to the formation of  $\text{Cd}(\text{OH})_2$  at pH greater than 5.8<sup>[25]</sup>. Cobalt was not removed at acidic pH 4, and its percentages remained nearly the same as those in the original samples during the two settling periods. More than 99.5% removal was achieved at moderate alkaline medium of pH 8, whereas 100 % removal occurred at pH10 during the extended settling period of 24-hour. The results obtained from the treatment at 2- and 24-hour periods are listed in Table 4 and 5.

*Table 4: The metal content of the atroun treated AMIW in mg/dm<sup>3</sup> after 2 hour settling time .*

Sample No.	pH of Treatment	Fe in mg/dm <sup>3</sup>	Mn mg/dm <sup>3</sup>	Zn mg/dm <sup>3</sup>	Cu mg/dm <sup>3</sup>	Cd mg/dm <sup>3</sup>	Co mg/dm <sup>3</sup>
S.1	pH 4	43680	523.68	3293.6	1258.9	10.10	45.40
S.1	pH 6	35616	517.88	1407.5	0037.7	9.00	39.95
S.1	pH 8	00000	010.65	0006.4	0001.8	0.10	00.28
S.1	pH 10	00000	002.07	0002.4	0001.2	0.60	00.13
S.2	pH 4	53460	208.76	1642.6	0995.2	7.10	33.43
S.2	pH 6	29568	178.76	1299.1	0066.2	6.40	27.48
S.2	pH 8	00000	008.68	0010.0	0001.5	0.10	00.26
S.2	pH 10	00000	002.41	0015.1	0001.2	0.30	00.04
S.3	pH 4	47712	188.80	1553.3	0550.9	5.90	46.23
S.3	pH 6	43008	178.16	1250.0	0024.6	5.50	42.58
S.3	pH 8	00000	002.64	0008.2	0001.5	0.00	00.21
S.3	pH 10	00000	003.14	0006.9	0000.6	0.60	00.06
S.4	pH 4	44352	204.12	1397.3	0265.6	4.90	38.96
S.4	pH 6	39648	186.76	1065.8	0014.3	4.00	34.78
S.4	pH 8	00000	003.86	0005.7	0001.0	0.10	00.17
S.4	pH 10	00000	000.80	0002.5	0000.4	0.30	00.04
S.5	pH 4	47712	235.16	1504.7	0466.6	6.30	45.88
S.5	pH 6	40992	218.96	1174.9	0016.4	5.50	39.78
S.5	pH 8	01344	002.29	0007.2	0001.7	0.10	00.19

S.5	pH 10	00000	009.88	0002.4	0000.5	0. 40	00.17
S.6	pH 4	00000	265.68	1623.4	0462.7	10. 30	04.21
S.6	pH 6	00000	248.12	1187.8	0031.4	5. 90	03.08
S.6	pH 8	00000	088.98	0021.9	0003.9	0.40	00.13
S.6	pH 10	00000	016.62	0006.6	0001.8	0.41	00.00

*Table 5: the metal content of the atroun treated AMIW in mg/dm<sup>3</sup> after 24 hour settling time .*

Sample No.; pH of Treatment	pH of Treatment	Fe in mg/ dm <sup>3</sup>	Mn in mg/ dm <sup>3</sup>	Zn in mg/ dm <sup>3</sup>	Cu in mg/ dm <sup>3</sup>	Cd mg/ dm <sup>3</sup>	Co in mg/ dm <sup>3</sup>
S.1	pH 4	43008	244.52	3193.6	590.76	10.86	46.56
S.1	pH 6	38304	215.84	1269.6	089.68	09.90	27.49
S.1	pH 8	00000	003.84	0004.4	003.21	0.064	00.17
S.1	pH 10	00000	001.44	0002.1	000.98	00.35	00.00
S.2	pH 4	53460	213.52	3208.0	0785.3	07.66	037.9
S.2	pH 6	30912	201.84	1264.6	077.42	06.52	032.2
S.2	pH 8	00000	001.44	0005.8	004.14	00.03	00.20
S.2	pH 10	00000	000.39	0001.3	002.14	00.02	00.00
S.3	pH 4	42336	195.08	2931.0	517.56	06.69	44.03
S.3	pH 6	43008	176.24	1068.0	082.24	05.79	26.57
S.3	pH 8	00000	000.68	0071.3	001.65	00.04	00.06
S.3	pH 10	00000	000.09	0000.9	001.36	00.24	00.00
S.4	pH 4	40992	213.76	1370.8	269.40	04.38	37.59
S.4	pH 6	37632	190.96	0938.1	056.62	04.20	22.90
S.4	pH 8	00000	000.78	0003.6	001.79	00.02	00.08
S.4	pH 10	00000	000.14	0001.9	000.80	00.04	00.00
S.5	pH 4	44352	224.12	2895.8	472.12	07.18	46.54
S.5	pH 6	36288	212.56	1065.7	016.32	05.44	27.06
S.5	pH 8	00000	000.48	0002.3	003.13	00.00	00.24
S.5	pH 10	00000	000.34	0001.7	001.95	00.23	00.00
S.6	pH 4	00000	254.20	3041.0	479.12	10.60	04.48
S.6	pH 6	00000	218.48	1258.8	008.46	08.22	03.24
S.6	pH 8	00000	079.74	0012.9	002.41	00.32	00.10
S.6	pH 10	00000	012.53	0006.2	002.04	00.46	00.16

According to parameters investigated, Ariab AMIW is considered as one of the highly contaminated effluents ever known in the world, though, its flow rate and quantity were not high. Treating industrial waste with local mineral resources increases the added value by introducing new utilization of local natural resources creating new market for the huge amounts of low grade atroun found in Darfour region which leads to new jobs for the natives. For these reasons Atroun was proposed for the treatment of AMIW to be used in the different processing operations.

The alkaline atroun treatment was chosen over biological passive techniques to treat the polluted Ariab AMIW under study, for many different reasons: high metals and anions load found in the water samples under study , high content of toxic elements detected , relatively low flow rate , high atmospheric temperature which is not suitable for the growth of ameliorating bacteria and microorganisms and predictive and controllable nature of active alkaline techniques.

The study proved that Atroun can be used in the treatment of AMIW and other industrial effluents in order to protect the environment from mining and industrial hazards. Moreover, the study introduced new utilization for the huge deposits of low grade atroun found northwest of the Sudan. The inherent alkalinity of the atroun was used to neutralize the high acidity, raise the AMIW pH and to precipitate the metal ions. Unfortunately sulphate content in the treated solutions

was increased due to the introduction of extra sulphate from the impure natural atroun. Nevertheless, the problem can be overcome by careful selection of low sulphate and chloride atroun, especially, when it is used for the AMIW treatment. Fortunately, iron, the major elemental pollutant was successfully removed at pH 8 and 10 at 2-hour settling period, mainly due to precipitation of iron as siderite ( $\text{FeCO}_3$ ) and hydroxide ( $\text{Fe(OH)}_3$ ). Manganese and zinc were not completely removed although high percentages removal was attained but the remaining Mn and Zn still need to be treated to conform with the effluent discharge regulations.

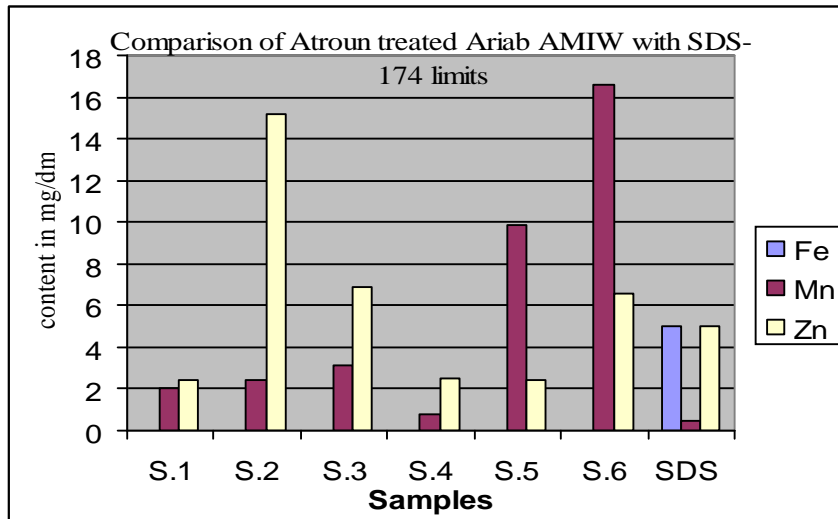
Excellent removal of copper and cobalt was attained at pH 9 in both settling periods. Cadmium, however, was removed to a good extent at pH 8, but it was slightly higher at pH 10, due to its tendency to dissolve at higher pH values. One of the disadvantages of the use of natural atroun was the presence of high sulphate and chloride levels in the ore in addition to incomplete removal of Zn and Mn after treatment.

The comparison of the atroun treated AMIW effluent parameters at pH 10 with those of local and international effluent discharge limits at both 2- and 24-hour settling periods is shown in table 6, Fig.1, 2, Table 7, Fig. 3 and Fig 4, respectively, which indicates that the net effluent conformed in most parameters with the allowed limits except in the case of sulphate, manganese and partially copper at 2-hour settling period.

*Table 6: Comparison of atroun treatment effluent parameters at pH 10 with discharge effluent limits at 2-Hour settling period*

parameter	S1	S2	S.3	S.4	S.5	S.6	SDS-174 limits
pH-value at 25C <sup>o</sup>	9.00	9.00	9.00	9.00	9.00	9.00	6 - 9
SO <sup>2-</sup> <sub>4</sub> in mg/dm <sup>3</sup>	244255	230405	282707	275338	337103	61483	350 max.
Fe in mg/dm <sup>3</sup>	0.00	0.00	0.00	0.00	0.00	0.00	5.0 max.
Mn in mg/dm <sup>3</sup>	2.07	2.41	3.14	0.8	9.88	16.62	0.50 max.
Zn in mg/dm <sup>3</sup>	2.40	15.16	6.9	2.5	2.4	6.60	5.0 max.
Cu in mg/dm <sup>3</sup>	1.20	1.20	0.60	0.40	1.7	1.80	1.0 max.
Cd in mg/dm <sup>3</sup>	0.60	0.30	0.60	0.30	0.40	0.41	---
Co in mg/dm <sup>3</sup>	0.13	0.04	0.06	0.04	0.17	0.00	0.50 max.

Comparison of Atroun treated Ariab AMIW with SDS



*Fig. 1: Comparison of Fe, Mn and Zn content of Atroun treated effluents at pH 10 for 2- hour settling period.*

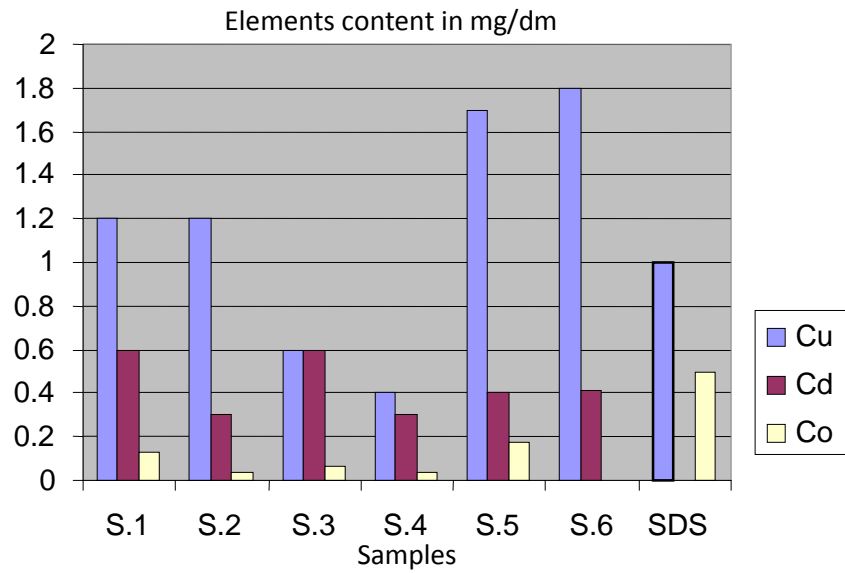


Fig. 2: Comparison of Cu, Cd and Co content of atroun treated effluents at pH 10 for 2- hours settling period

Table 7: Comparison of atroun treatment effluent parameters with at pH 10 with SDS -174 discharge effluent limits at 24- hour settling period.

parameter	S.1	S. 2	S.3	S.4	S.5	S.6	SDS-174 limits
pH-value at 25 °C	9.00	9.00	9.20	9.00	9.00	8.70	6 - 9
SO <sub>4</sub> <sup>-2</sup> in mg/dm <sup>3</sup>	310655	271763	289656	279675	241963	052244	350 max.
Fe in mg/dm <sup>3</sup>	0.00	0.00	0.00	0.00	0.00	0.00	5.0 max.
Mn in mg/dm <sup>3</sup>	1.44	0.39	0.10	0.20	0.34	12.53	0.50 max.
Zn in mg/dm <sup>3</sup>	2.10	1.30	0.90	1.90	1.70	6.20	5.0 max.
Cu in mg/dm <sup>3</sup>	0.98	2.14	1.40	0.80	1.95	2.04	1.0 max.
Cd in mg/dm <sup>3</sup>	0.35	0.02	0.14	0.04	0.23	0.46	---
Co in mg/dm <sup>3</sup>	0.17	0.00	0.00	0.00	0.00	0.16	0.50 max.

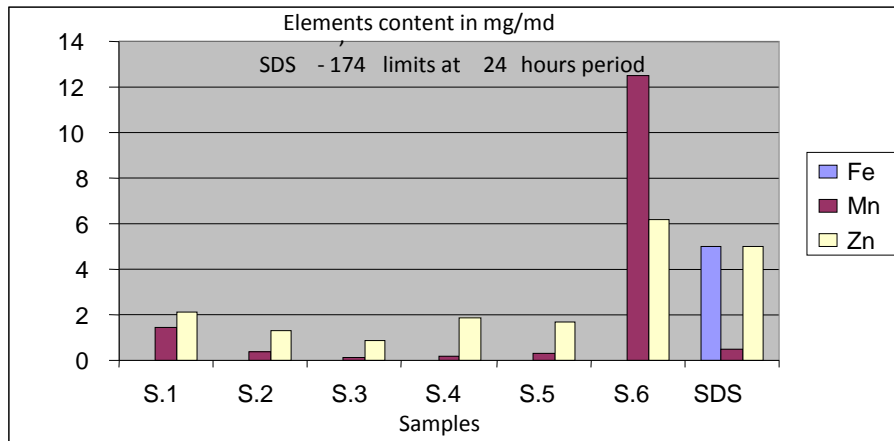


Fig. 3: Comparison of Fe, Mn and Zn content of Atroun treated effluents at pH 10 for 24 hours period

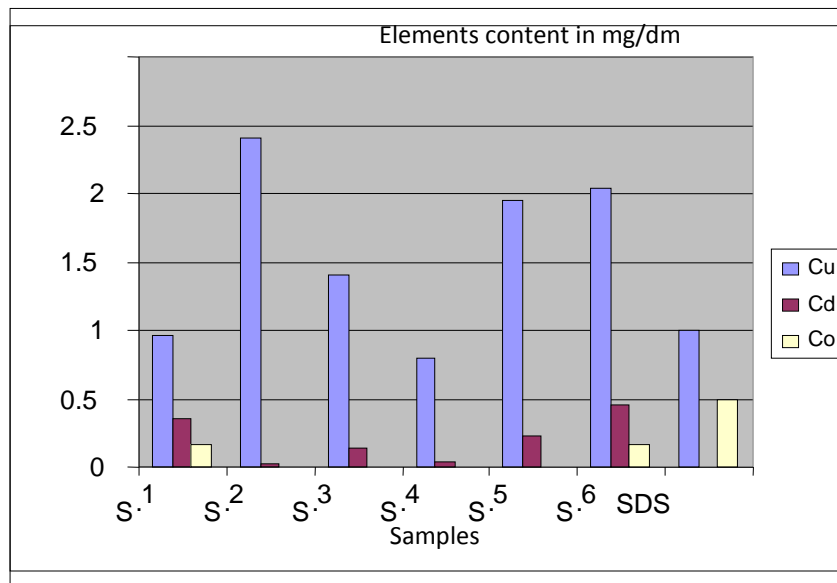


Fig. 4: Comparison of Cu, Cd and Co content of atroun treated effluents at pH 10 for 24-hours settling period

## CONCLUSIONS

Chemical treatment of Ariab acidic mine-influenced water (AMIW) with Sudanese trona (atroun) was effective in the removal of acidity and heavy metals, to the standard discharge limits of industrial waste water, except in the reduction of sulphate, and to some extent manganese and zinc in few treated samples.

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